

Cu-Sb dumbbell arrangement in the spin-orbital liquid candidate $\text{Ba}_3\text{CuSb}_2\text{O}_9$

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(Dated: January 19, 2017)

The absence of both spin freezing and of a static Jahn-Teller effect have lead to the proposition that $\text{Ba}_3\text{CuSb}_2\text{O}_9$ is a quantum spin-orbital liquid. However, theoretical understanding of the microscopic origin of this behavior has been hampered by a lack of consensus on the lattice structure. Cu ions have been proposed to realize either a triangular lattice, a short-range ordered honeycomb lattice or a disordered lattice with stripe-like correlations. Here we analyse the stability of idealized versions of these arrangements using density functional theory. We find stripe order of Cu ions to be energetically favoured, which is strongly suggestive that the local Cu-Cu arrangement in the disordered materials is stripe-like. Furthermore, we find evidence of significant interlayer interactions between Cu-Sb dumbbells, which affects the out-of-plane arrangement. Analysis of the relaxed crystal structures, electronic properties and tight-binding parameters provides clues as to the nature of the Jahn-Teller distortions.

I. INTRODUCTION

In recent years there has been an enormous amount of effort devoted to the search for materials with quantum spin liquid phases.^{1–8} A special class of quantum liquids are those where not only the spins but also the orbitals remain disordered and fluctuating at low temperatures, resulting in a spin-orbital liquid state.^{9–13}

Recently, $\text{Ba}_3\text{CuSb}_2\text{O}_9$ has been suggested as a promising candidate to realize spin-orbital liquid behavior.^{14–22} Thermodynamic measurements^{14,15}, μSR ¹⁶ and neutron scattering experiments¹⁵ find no spin ordering or spin freezing down to temperatures as low as 20mK. Electron spin resonance (ESR) and x-ray diffraction measurements find no evidence of a cooperative Jahn-Teller transition, implying that, not only spins, but also orbitals fail to order.¹⁵ Furthermore, variable frequency ESR measurements suggest that the Jahn-Teller distortions remain dynamic down to low temperatures, rather than simply freezing and forming a glass-like arrangement.¹⁹ This implies that the orbital degrees of freedom fluctuate at low temperature, and the ESR measurement of the timescale of this fluctuation is consistent with extended x-ray absorption fine structure (EXAFS) and x-ray measurements¹⁵.

While the spin and orbital degrees of freedom in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ are primarily associated with the Cu ions, the important sub-units of the system are $\text{Cu}^{2+}\text{-Sb}^{5+}$ charged dumbbells surrounded by oxygen bi-octahedra (see Fig. 1). These dumbbells form a triangular lattice and two orientations of the dumbbell are possible, with either Cu or Sb on top. Despite intensive experimental and theoretical investigations, no clear consensus has been reached so far on the arrangement of these dumbbells. Such a knowledge is necessary in order to unveil the microscopic origin of the spin-orbital liquid behavior.^{23–25} There have been three main proposals: (i) The dumbbells have all the same orientation and the Cu ions thus form a triangular lattice;^{14,26} (ii) The dumbbells are disordered but form a honeycomb struc-

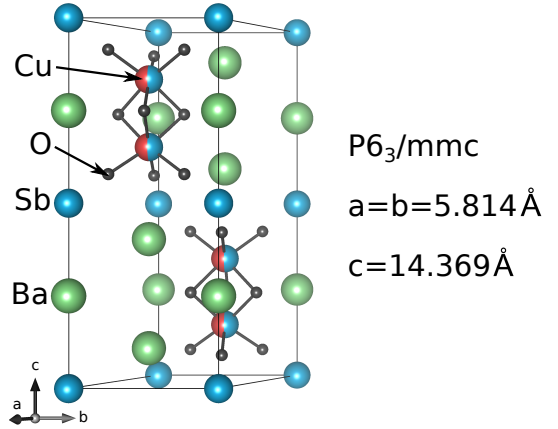


FIG. 1. The crystal structure of $\text{Ba}_3\text{CuSb}_2\text{O}_9$, as revealed by x-ray and neutron diffraction experiments¹⁵. Cu-Sb dumbbells (red/blue) form a triangular lattice, but each dumbbell is in one of two possible orientations, with either the Cu or Sb ion on top. Experimentally, in the absence of long-range order, it is difficult to determine the local arrangement of the dumbbells.

ture at short lengthscales;¹⁵ (iii) A stripe structure of Cu spins is energetically favorable with the dumbbells freezing in a disordered state with short-range stripe-like correlations.²⁵

In this work we compare these different options via density functional theory (DFT) calculations of idealized, long-range-ordered dumbbell arrangements with different three-dimensional stackings and show that the stripe configuration (iii) has the lowest energy. Even though in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ the dumbbells are disordered, our results hint at stripe-like arrangements at the local level²⁵ and suggest that if a real material is cooled sufficiently slowly from the synthesis temperature, one should expect a long-range stripe order of the dumbbells. Finally, starting from the idealized structure with long-range dumbbell order, we discuss both the nature of the expected Jahn-Teller distortion and the electronic properties.

II. CRYSTAL STRUCTURES

A number of different arrangements of $\text{Cu}^{2+}\text{-Sb}^{5+}$ dumbbells have been proposed in the past and it is useful to summarize the evidence for each of these.

Historically, $\text{Ba}_3\text{CuSb}_2\text{O}_9$ was proposed to crystallize in the centrosymmetric space group $P6_3mc$, and to have a parallel alignment of the dumbbells,^{14,26} so that the Cu ions form a triangular lattice. However, this arrangement would be associated with a large electrical dipole moment and is not consistent with pyroelectric measurements.¹⁵ Furthermore, previous DFT calculations showed that this arrangement was energetically unfavorable with respect to honeycomb dumbbell arrangements.²⁷

Additional work on the refinement of the crystal structure suggested that the space group is the centrosymmetric $P6_3/mmc$.¹⁵ The appearance of partial occupancies of Cu/Sb positions implies that there is no long-range ordering of the dumbbells, but one expects an equal number of dumbbells in each orientation so as to be compatible with the absence of internal dipole moments observed in pyroelectric measurements. X-ray diffraction data show no Bragg peaks associated with the dumbbell ordering, confirming that the dumbbells are disordered.¹⁵ Diffuse x-ray scattering measurements suggest short-range honeycomb order of the dumbbells, in which the central dumbbell of a hexagonal plaquette is oriented anti-parallel to the other dumbbells.¹⁵ However, it should be noted that the approximate domain size was found to be ~ 10 Å, which is less than twice the spacing between neighbouring dumbbells. The proposal of honeycomb short-range order inspired a number of theoretical studies of the spin and orbital physics, but it was found that long-range orbital order is difficult to avoid.^{23,24}

Finally, a recent theoretical study proposed that the lowest-energy dumbbell arrangement consists of stripes, with a parallel dumbbell alignment within each stripe and antiparallel alignment between neighbouring stripes.²⁵ This suggestion was based on solving a highly simplified 2D model, in which dumbbells interact only via their charge degrees of freedom. It was further discussed that the materials do not reach this ground state configuration, but instead freeze into a disordered configuration with short-range, stripe-like correlations, dubbed a “branch” lattice. This picture was found to be consistent with the x-ray diffraction data reported in Ref. [15], which was initially taken as evidence of a honeycomb structure, as well as an x-ray study of the pair distribution function.²⁰ In fact this “branch” lattice is naturally tuned to a percolation critical point and preliminary calculations suggest that this type of correlated disorder could drive the formation of a spin-orbital liquid.²⁵ There is a clear need for a first-principles calculation to evaluate whether such a stripe-ordered configuration is indeed lower in energy than other competing structures.

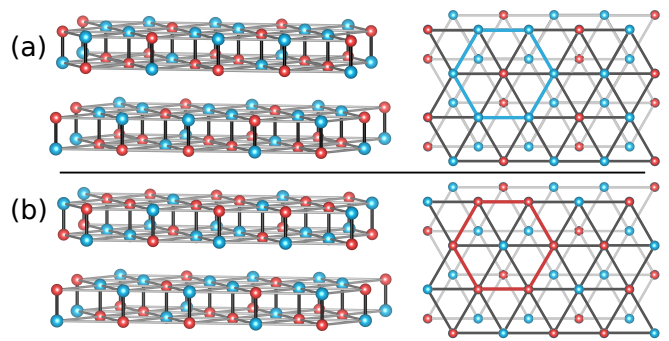


FIG. 2. The two honeycomb arrangements of Cu-Sb dumbbells taken as starting points for the density functional theory calculations. Cu ions are shown in red and Sb in blue. (a) Side and top views of the *honey-a* structure, which has a net dipole moment. (b) Side and top views of the *honey-b* structure, where the upper plane has been flipped with respect to the *honey-a* structure. In the *honey-b* structure the net dipole moment cancels between neighbouring planes.

III. METHODS

We perform DFT calculations within the generalized gradient approximation (GGA), the spin-polarized GGA and GGA+U, starting from a set of idealized crystal structures with different dumbbell ordering patterns. For each structure we relax the internal coordinates²⁸ using the projector augmented wave method, as implemented in the Vienna ab initio simulation package (VASP²⁹). As the lattice parameters have been confirmed in several measurements^{14,15,26} we keep them fixed to their experimental values. We have verified that our results remain valid also in the case of a full relaxation.²⁷ The total energies were checked using the all-electron full-potential localized orbital code (FPLO³⁰), which was also employed to calculate the electronic band structures and density of states.

In previous DFT studies correlation effects were found to play an important role, not only to achieve insulating behavior, but also to allow for the formation of distinct Jahn-Teller distortions of the oxygen octahedra.²⁷ Here we compare our GGA calculations to Coulomb corrected GGA+U simulations, where the correlations on the Cu atoms are explicitly included via a Hubbard term.³¹ We choose $U = 4$ eV in accordance with previous studies.²⁷ The total energies are converged on a $6 \times 6 \times 6$ and $4 \times 4 \times 4$ k mesh for the stripy and honeycomb arrangement of the dumbbells, respectively.

IV. COMPARISON OF ENERGIES

In order to discern which of the proposed dumbbell arrangements is lowest in energy, we consider four different structures with long-range dumbbell order, shown in Fig. 2 and Fig. 3, relax their internal coordinates, and compare their energies. Although in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ the

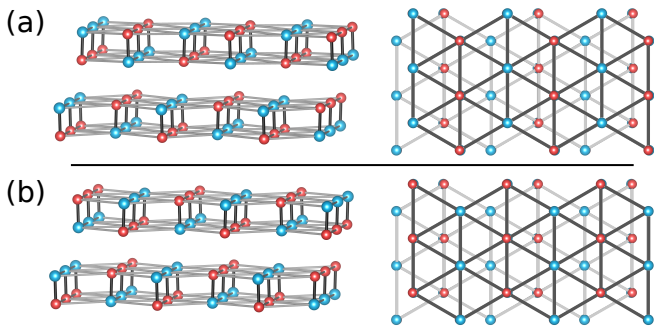


FIG. 3. The two stripe arrangements of Cu-Sb dumbbells taken as starting points for the density functional theory calculations. Cu ions are shown in red and Sb in blue. (a) Side and top views of the *stripy-a* structure. This configuration is chosen so as to minimize the energy of the electrostatic interaction between neighbouring planes. (b) Side and top views of the *stripy-b* structure, where the upper plane has been flipped with respect to the *stripy-a* structure.

dumbbells are not long-range ordered, the energy difference between these idealized structures will give us a strong indication as to the type of local correlations in the system.

The first structure we consider, *honey-a*, has a ferrimagnetic honeycomb arrangement of the dumbbells in each layer in the sense that there is a 2:1 ratio between the two dumbbell orientations (Fig. 2(a)). The neighbouring layers are chosen to have the same ferrimagnetic ordering with a resulting net dipole moment associated with the configuration. This arrangement was considered in Ref. [27] and it was found to be energetically favorable over the parallel alignment of all dumbbells.

The second structure, *honey-b*, has the same honeycomb arrangement in the layers as *honey-a* but the stacking of layers is such that there is no net dipole moment (Fig. 2(b)). From a naive electrostatic picture this would appear to be higher in energy than *honey-a*. However, this consideration doesn't take into account the exchange energy, and, as noted in Ref. [15], interlayer exchange pathways between Cu ions at the top of the lower layer and bottom of the upper layer are comparable with those within the layers, and thus could be important.

The third structure, *stripy-a*, has a stripe arrangement of the dumbbells in each layer (Fig. 3(a)). The interlayer stacking is chosen such as to minimize the electrostatic energy between neighbouring layers.

The fourth structure, *stripy-b*, also has a stripe arrangement of the dumbbells in each layer (Fig. 3(b)). However, a different interlayer stacking is chosen, which is the only period-2 alternative to *stripy-a*, assuming that stripes in neighbouring layers run parallel to one another.

Comparing the total energies of the two honeycomb structures, we find that *honey-a* has a considerably lower energy than *honey-b* of about 30 meV per formula unit (see Fig. 4). This is in agreement with naive electrostatic considerations, and shows the importance of the interlayer effects on the dumbbell structure.

The *stripy-a* and *stripy-b* structures are, interestingly,

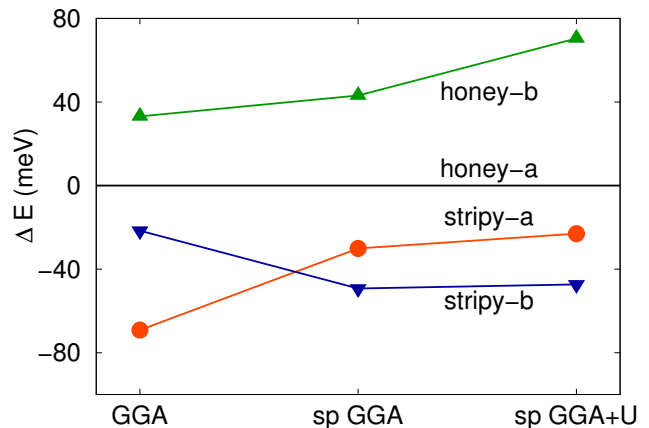


FIG. 4. Total energy per formula unit of different dumbbell configurations, measured relative to that of the *honey-a* structure (see Fig. 2(a)). Three different functionals are used, non spin-polarized GGA, spin-polarized GGA and GGA+U in a ferromagnetic setup, and these give broadly consistent results. The lowest energy configuration is found to be the *stripy-b* structure (see Fig. 3(b)).

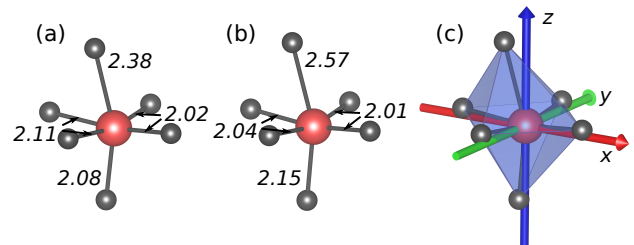


FIG. 5. Local arrangement of the oxygen (grey) octahedra surrounding a Cu ion (red). The Jahn Teller distortion as obtained in the spin-polarized GGA relaxation of the (a) *stripy-a* and (b) *stripy-b* structure (see Fig. 3). The JT distortion is more pronounced in the *stripy-b* structure with 1 long bond of 2.57 Å, and 5 shorter bonds of between 2.01 – 2.15 Å. (c) The local coordinate system used to derive the orbital contribution to the bands.

considerably lower in energy than *honey-a* by at least 20 meV per formula unit (see Fig. 4). When using pure GGA, the *stripy-a* structure is lower in energy than *stripy-b*, as expected from a simple electrostatic picture. However, spin-polarized GGA and spin-polarized GGA+U show that exchange effects favour the *stripy-b* structure, and the energy is better by approximately 20 meV per formula unit.

Thus, *stripy-b* has the lowest energy, which is strongly suggestive that local correlations will be of this type in the material.

V. JAHN-TELLER EFFECT

One of the most interesting, and most discussed, aspects of $\text{Ba}_3\text{CuSb}_2\text{O}_9$ is the nature of the Jahn-Teller effect, which is believed to provide information about the orbital occupancies. Probes of the Jahn-Teller effect that

operate on short timescales, such as EXAFS¹⁵ and Raman spectroscopy¹⁸ see a static distortion at low temperature. However, slower probes, such as x-ray diffraction¹⁸ see a dynamic Jahn-Teller effect. These observations have been shown to be consistent by performing variable frequency ESR measurements, which determine a dynamic Jahn-Teller timescale of about 100ps.¹⁹ Measurements that probe the system on a shorter timescale naturally see a static distortion.

In the idealized, long-range ordered *stripy-b* structure, we find that there is a static Jahn-Teller distortion, and this is independent of the choice of functional. One of the six Cu-O bonds is considerably longer than the other five, and the bond lengths are shown in Fig. 5(b). The bond opposed to the long bond is found to be slightly larger than the bonds lying in the perpendicular plane. In the *stripy-a* structure, the Jahn-Teller distortion is similar, but a little less pronounced (see Fig. 5(a)).

VI. ELECTRONIC PROPERTIES

DFT calculations give access not only to the nature of the crystal structure, but also to the electronic band structure.

Common electronic properties of all considered crystal structures are: (i) a strong e_g - t_{2g} splitting of the Cu 3d orbitals; (ii) a Jahn-Teller distortion which induces splitting of the partially filled e_g bands; (iii) the bands near the Fermi level are predominantly of $d_{x^2-y^2}$ and d_{z^2} character, but there are also small contributions from the oxygen p orbitals and, due to additional distortions of the octahedra, from Cu t_{2g} orbitals.

The band structure associated with the *stripy-a* structure is shown in Fig. 6(a). At the level of spin-polarized GGA, there is no gap. In such a case it is not unreasonable that additional correlation effects could drive a dynamic Jahn-Teller distortion.

The band structure of the *stripy-b* structure is shown in Fig. 6(b), and shows considerable differences from the case of the *stripy-a* structure, demonstrating the importance of the interlayer dumbbell arrangement. In particular, there is a gap of about 0.5 eV between the e_g bands already at the level of spin-polarized GGA calculations. Using the local coordinate system shown in Fig. 5(c), we observe that the band with predominantly d_{z^2} character is fully occupied, while the $d_{x^2-y^2}$ minority-spin band is empty. The large energy separation between these bands suggests that a dynamic Jahn-Teller effect cannot occur in the idealized *stripy-b* structure.

The static Jahn-Teller distortion predicted for the *stripy-b* structure is in contrast to measurements of a dynamic Jahn-Teller distortion in the material.¹⁹ This suggests that the dynamic nature of the Jahn-Teller distortion is driven by the presence of dumbbell disorder, which is not taken into account in the DFT calculations. While the presence of disorder does not necessarily imply a dynamic Jahn-Teller distortion, a plausible scenario for

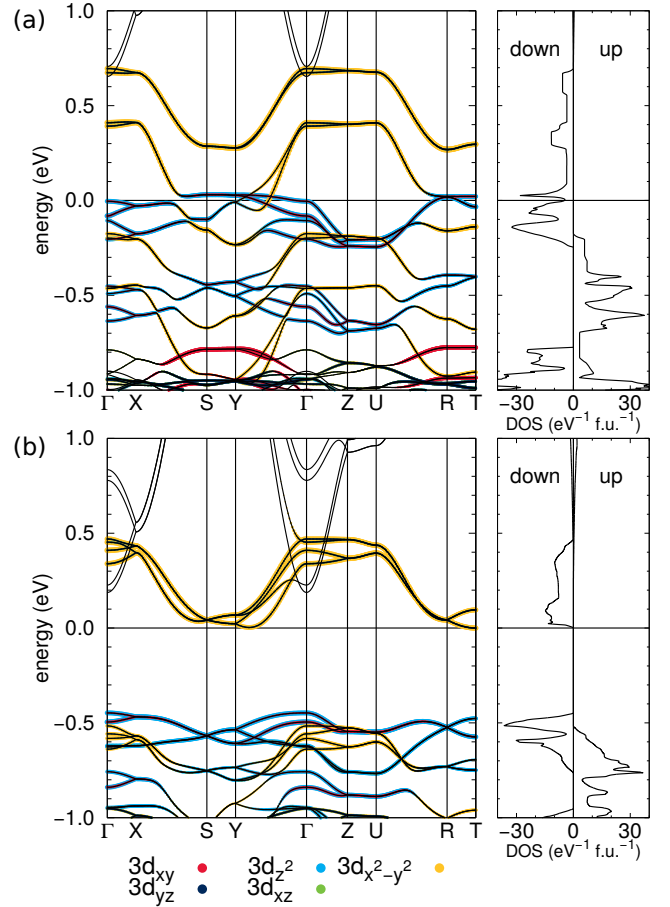


FIG. 6. Band structure and density of states of $\text{Ba}_3\text{CuSb}_2\text{O}_9$, calculated using spin-polarized GGA. (a) Band structure associated with *stripy-a* dumbbell ordering (see Fig. 3(a)). (b) Band structure associated with *stripy-b* dumbbell ordering (see Fig. 3(b)). The colour scheme assigns a predominant character to the bands associated with the Cu d electrons. The density of states is shown on the right-hand side.

how it could result in a dynamic Jahn-Teller distortion has been proposed in Ref. [25].

Finally, we also determined via Wannier functions³⁰ the tight-binding parameters associated with the different crystal structures. In both the *stripy-a* and *stripy-b* structures, the dominant intralayer hopping path for the single hole in the e_g band is along the stripe direction, and mediated by the $d_{x^2-y^2}$ orbitals. Hopping between neighbouring stripes within the same layer is highly suppressed, and this is in agreement with a simple analysis of exchange pathways^{15,24}. The main difference between the *stripy-a* and *stripy-b* structures is unsurprisingly in the interlayer hopping. In the *stripy-a* the lobes of the $d_{x^2-y^2}$ orbitals in neighbouring layers point towards each other, yielding hopping integrals as high as $t \gtrsim 150$ meV. In the *stripy-b* structure this is not the case, and the interlayer hopping is highly suppressed relative to the *stripy-a* case.

VII. SUMMARY

Using DFT we have explored how Cu-Sb dumbbells are arranged in the quantum spin-orbital liquid candidate $\text{Ba}_3\text{CuSb}_2\text{O}_9$. This involved a comparison between different idealized dumbbell arrangements, and it was found that an in-plane stripe arrangement is considerably lower in energy than other candidate structures. This strongly suggests that in real crystals, which have dumbbell disorder, the local correlations are stripe like, as predicted in Ref. [25].

We have also demonstrated the importance of the interlayer arrangement of the dumbbells, which is most noticeable in the electronic band structure. The lowest energy structure, *stripy-b*, has a large gap of approximately 0.5 eV at the Fermi level, and it is therefore hard to conceive that correlation effects could drive a dynamic Jahn-Teller distortion in the idealized crystal. This in turn suggests the importance of disorder to explain the observed dynamic Jahn-Teller distortion.²⁵

By clarifying the arrangement of the Cu ions in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ we hope to provide a good starting point for theories that aim to understand the nature of the experimentally observed spin and orbital fluctuations.

ACKNOWLEDGMENTS

We thank L. Balents, C. Broholm and S. Nakasutji for useful discussions. MA and RV thank the German Research Foundation (Deutsche Forschungsgemeinschaft) for support through grant SFB/TR49. AS and FM thank the Swiss National Science Foundation and its SINERGIA network “Mott physics beyond the Heisenberg model” for financial support. MA, FM and RV further acknowledge partial support by the Kavli Institute for Theoretical Physics at the University of California, Santa Barbara under National Science Foundation Grant No. PHY11-25915.

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